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INFLUENCE OF SOME AGGRESSIVE MEDIA ON CORROSION RESISTANCE OF MORTARS WITH SPENT CRACKING CATALYST

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Abstract

The influence of spent catalyst from catalytic cracking in fluidized bed on the hydration process of cement and the properties of cement mortars were studied. The spent catalyst was used as an additive to cement in the mortars (10 and 20% of cement). The samples of mortars kept in water for 28 days, then they were placed in sulfate and chloride media for 2 months (the control samples were kept in water for 3 months). After this time they were subjected to bending strength and compressive strength determinations. Thermogravimetric and infrared absorption studies were performed and capillary elevation, capability of binding heavy metals, and changes in mass and apparent density were determined too. The studies disclosed the pozzolana nature of spent catalyst and its influence on cement mortars being in contact with corrosive media.

Keywords: cement mortars, corrosion resistance of mortars, hydration of cement, pozzolana additive

Introduction

The mixing of cement with water gives rise to complex processes of hydration and hydrolysis which depend i.a. on mineral composition of the binder, water-to-cement ratio, temperature and humidity of environment, and grain size of cement particles. The main products of hydration are hydrated calcium silicates (the so-called C–S–H phase), hydrated aluminates, aluminosilicates, and aluminoferrates of calcium, and calcium hydroxide. In the presence of pozzolana additives, containing active silica, the amount of $Ca(OH)_2$ in the system decreases as a consequence of binding with the pozzolana compound and transition to the C–S–H gel. The addition of finely ground pozzolana material to cement may increase the impermeability to water and improve the corrosion resistance of mortars and concretes. No doubt, that in the case of reinforced concrete structures there must be a certain optimum amount of pozzolana additive because of the passivating effect of $Ca(OH)_2$ to steel. Therefore, a spent catalyst from catalytic cracking in fluidized bed (fluidized bed cracking catalyst – FBCC) seems to be a good pozzolana additive due to its chemical composition and high dispersion degree.

In the presence of sulfates cement slurries undergo chemical reactions leading to formation of expansive gypsum and ettringite in proportions depending on the concentra-

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tion of SO_4^{2-} ions [1–3]. Some sulfates also lead to the decomposition of the C–S–H phase. The resistance of concrete to sulfate aggressiveness depends largely on the mineral composition of cement. High resistance is an effect of small contents of C_3A phase and moderate contents of C_3S, owing to which considerable amounts of calcium hydroxide are formed [4]. An increase of resistance to aggressive sulfate waters may be attained by the introduction of pozzolana additives, which lead to the decrease of $Ca(OH)_2$ content and to the increase of the amount of C–S–H phase. However, the additives may not contain excessive amounts of aluminum compound that would lead to the formation of hydrous calcium aluminates. It is extremely important in case under consideration because of the abundance of aluminum compounds in the spend catalyst.

In case of reinforced concrete constructions a problem of primary importance is the susceptibility of concrete to the action of chlorides which depassivate the steel surface [5, 6], although it is not taken into account in the standard classification of aggressive media for concrete [7]. The chloride aggressiveness is connected mainly with the use of defrosting agents, the harmful effect of which consists in formation of new phases with calcium hydroxide and considerable lowering of pH of the slurries. The destructive effect is particularly intense in concretes containing large amounts of portlandite.

In this work attempt was made to survey the mechanism of pozzolana action of FBCC on cement mortars being in contact with sulfate and chloride media by means of thermogravimetric methods and infrared spectroscopy. In addition, water impermeability was determined for mortars with different contents of FBCC, and their mechanical strength after short contact with aggressive media and with water environment was evaluated.

Experimental

The studies were carried out with Portland cement and FBCC of chemical and mineralogical compositions given in Table 1, standard sand, and solutions of chlorides (NaCl 225 and $MgCl_2 \cdot 6H_2O$ 25 g dm^{-3}) and sulfates (SO_4^{2-} 1250 mg dm^{-3}).

In the mortars used FBCC was used to replace 10 or 20% of cement, the water/binder ratio was 0.5, and sand/binder ratio was 3.0. The mortars were formed in standard shapes dimensions 4×4×16 cm for determination of mechanical strength [8, 9]. The samples were formed in 3-piece moulds, thickened in vibrators, the moulds were opened in 24 h, and the samples kept in water for 28 days. Then they were placed in corrosive media for 2 months, after which they were subjected to bending strength (R_f) and compressive strength (R_c) determinations.

Thermogravimetric and infrared absorption studies were performed with ground samples, free of coarser sand grains, triturated to particle size <0.3 mm. Analytical samples were taken in 28 days, from mortars kept in water, and in 3 months – from mortars kept in water and in chloride and sulfate environments. In case of aggressive media the samples were taken from the surface layer, the most exposed to the action of aggressive agents. For the sake of comparison IR absorption spectra were recorded also for individual components of the mortars: cement, FBCC, and sand. Thermogravimetric studies were carried out by means of Derivatograph C (MOM Budapest)

Table 1 Chemical and mineralogical composition and some properties of the materials studied, as well as some ASTM requirements concerning pozzolana additives [10]

Cement		FBCC		Pozzolana additive conform to ASTM	
Chemical composition/%	Mineralogical composition/%	Chemical composition/%	Physical properties	Chemical composition/%	Physical properties
CaO 64.2	C_3S 70.28	CaO 0.26	Sp. surface	min. 70 for	max. 34%
SiO_2 19.2	C_2S 2.10	SiO_2 55.89	105 $m^2 g^{-1}$	SiO_2+Al_2O_3+	residue on
Al_2O_3 5.0	C_3A 9.36	Al_2O_3 38.80	max. 28%	Fe_2O_3.	45 µm sieve
Fe_2O_3 2.3	C_4AF 6.99	Fe_2O_3	residue on	humidity	
SO_3 2.9	$C\overline{S}H_2$ 6.24	SO_3 1.73	40 µm sieve	max. 3	
MgO 1.6		MgO 0.03		ignition loss	
		Humidity 0.6		10	
		Ignition loss 1.5			
Specific surface 0.25 $m^2 g^{-1}$					

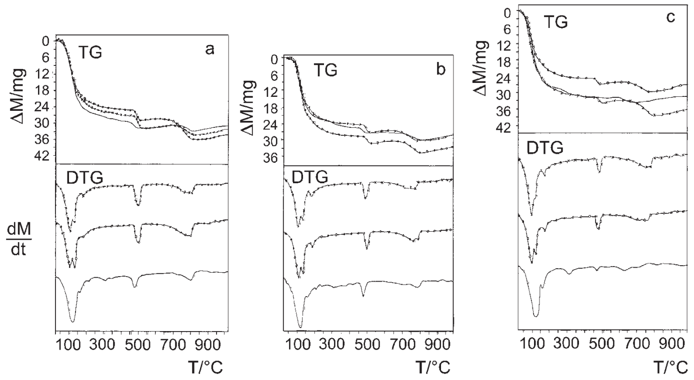

Fig. 1 Comparison of TG and DTG of cement mortars (surface layers) kept in: water (-x-x-), SO_4^{2-} (-o-o-o-o-) and Cl^- (----). a – control mortar, b – mortar containing 10% of FBCC, c – mortar containing 20% of FBCC

in temperature range 50–1000°C in air atmosphere. The IR spectra were recorded in Specord 75 IR Spectrophotometer, Karl Zeiss, Jena.

In addition, absorbability, capillary elevation, capability of binding heavy metals, and changes in mass and apparent density were determined for samples kept in aggressive media. The depth of penetration of soluble chlorides was determined after staining mortar fractures with 0.1 N $AgNO_3$ which were then photographed, according to an Italian Standard [11].

Discussion of results

An example of the results of thermogravimetric studies is given in Fig. 1. The TG curves were used for estimation of the content of calcium hydroxide in the mortars from the loss in mass at 500°C corresponding to the decomposition of $Ca(OH)_2$ (Fig. 2). Samples of 28-day mortars containing FBCC additive and kept in water contained much less

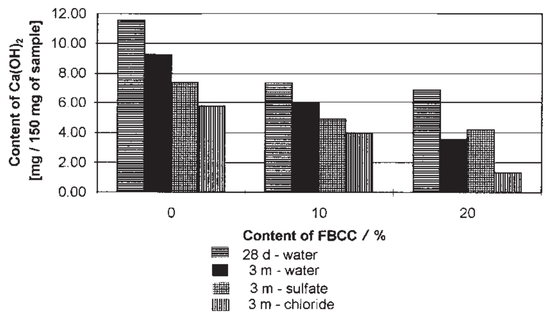

Fig. 2 Contents of $Ca(OH)_2$ in cement mortars kept for 28 days in water (deep layers) and for 3 months in environments: water, SO_4^{2-} and Cl^- (surface layers)

Table 2 Absorbability (n_m), capillary elevation in 28-day mortar samples, concentration of heavy metals in cultivating solutions and depth of penetration of Cl^- ions (h_{Cl}) after 3-month storage of mortars with various amounts of FBCC in chloride solutions

FBCC content/%	Apparent density/g cm^{-3}	n_m/%	Capillary elevation								h_{Cl}/mm		Conc. in cultivating solns.*/μg l^{-1}	
			mass increase/%				height of humidity zone/mm							
			1 h	3 h	6 h	24 h	1 h	3 h	6 h	24 h	min.	max.	Ni	V
0	2.08	7.89	0.48	0.79	1.08	2.17	4.8	8.3	9.8	27.9	13	23	0.4	2.6
10	2.05	8.06	0.38	0.68	0.92	1.93	4.5	7.7	9.0	15.1	7	13		
20	2.00	8.49	0.25	0.50	0.73	1.69	5.8	8.3	10.0	15.3	5	8	2.0	0.5
100	water extract 1:10												900	220

*Mass ratio of mortar:water=1:10

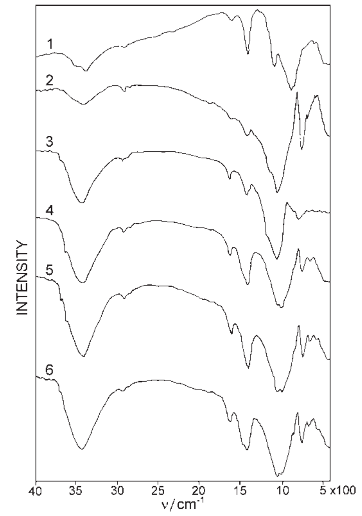

Fig. 3 Comparison of infrared absorption spectra of cement mortars components and cement mortars (surface layers) kept in chloride environment; 1 – portland cement, 2 – sand, 3 – FBCC, 4 – mortar containing 0% addition of FBCC, 5 – mortar containing 10% addition of FBCC, 6 – mortar containing 20% addition of FBCC

$Ca(OH)_2$, as compared with the control sample, probably due to the action of the pozzolana material added. As it may be guessed per analogy to naturally occurring pozzolana, the crystalline zeolite, the pozzolana effect of the spent catalyst used may be reduced to its dissolving in the slurry. The process of binding $Ca(OH)_2$ from the liquid phase proceeds rapidly and pozzolana is converted to an aluminosilicate gel [3]. Thermogravimetric studies of mortars kept in SO_4^{2-} and Cl^- environments exhibit clearly their effect on the hydration process due to leaching of some slurry components and/or chemical reactions of environmental anions with slurry components in the mortars. Particularly strong leaching effect was observed in mortars containing 20% additions of FBCC kept in concentrated solutions of chlorides or even in tap water. More precise in-

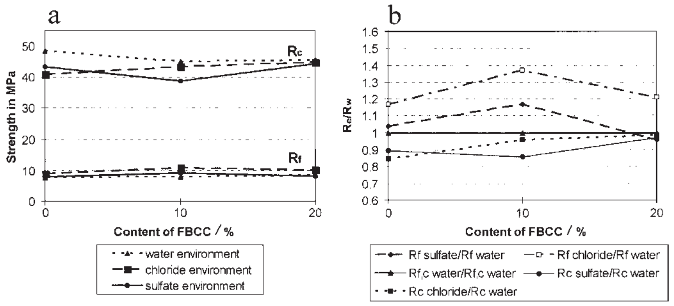

Fig. 4 Influence of FBCC addition on average bending strength – R_f, average compression strength – R_c (a) and susceptibility to corrosion (b) of the mortars kept for 3 months in water, sulfate and chloride media

terpretations may be expected from mortars subjected to a long term action of aggressive environments. Comparison of TG and DTG curves (Fig. 1) taken for mortars kept in identical media shows that the amount of FBCC additive has no substantial effect on the quality of the hydration products obtained. In the surface layers of 3-month mortars kept in aggressive media the content of $Ca(OH)_2$ was lower in samples modified with FBCC. It results probably from the complex action of FBCC, interaction of calcium hydroxide with anions from the solution and carbonization processes. Account should also be given to the leaching effect of water on the mortars.

The IR spectra of cement mortars exhibit no substantial differences. An example of comparison of IR spectra of mortars modified with different amounts of FBCC and kept in a medium containing aggressive Cl^- is shown in Fig. 3. Comparative studies of IR spectra of surface and deep layers of mortars kept in sulfate environments show some differences due to the different intensity of an absorption band characteristic for $Ca(OH)_2$. This may be accounted for increased content of calcium hydroxide in the control mortar, as compared with an FBCC-containing mortar, the $Ca(OH)_2$ band in the deep layers being much more intensive. There is no clear absorption band characteristic for the sulfates, which probably may be accounted for the masking by bands due to other mortar ingredients, e.g. sand.

Investigation of changes in mass and in apparent density of mortars kept in water and in aggressive media has shown that only chlorides give rise to mass increase, probably due to inclusion in the near-surface layer or due to reaction with $Ca(OH)_2$. This increase in sample mass is smaller in mortars containing 10 or 20% FBCC (0.78 and 0.57%, respectively) than in the control sample (0.94%).

Studies of absorbability and capillary elevation show that in the 28-day mortars the absorbability due to open pores and thus the overall porosity of the mortars increase with increasing contents of FBCC additive. On the other hand, the capillary elevation decreases markedly, probably because of lower contents of the C–S–H phase than in the FBCC-free mortars. It should be pointed out, however, that the porosity depends on the w/c ratio and on the thickening of the mortars. In the mortars studied , in the absence of surface active agents, the addition of finely dispersed FBCC (specific surface 105 $m^2 g^{-1}$) was associated with changes in consistence of the mortars that might influence their water tightness. Besides, on designing the mortars assumption was made that the water/binder ratio is 0.5. In practice, however, the water/cement ratio is much higher, which may result in increased porosity. Hence one may conclude that FBCC does not substitute cement in the mortars. A decrease of porosity may be achieved by an appropriate addition of surface active agents to enable proper thickening of the mortar without modification of the water/binder ratio.

However, the study of the depth of chloride penetration and concentration of Ni and V in the cultivating solutions being in contact with the mortars show that FBCC additions increase the water tightness of the mortars and the thickness of the layer of soluble chlorides is the highest in mortars with 0 addition of FBCC (Table 2).

The results of strength tests of mortars containing FBCC additives, kept in various media, are shown in Fig. 4. Bending and compression strength tests show that the presence of FBCC has no negative effect on the strength of the mortars despite of the problems connected with composition and preparation of the mortars.

Observations of 3-month action of corrosive media on the mortars have shown that:

– within the range of concentrations studied the effects of Cl^- and SO_4^{2-} ions on the mortars were similar. In either case a small decrease of compressive strength and a small increase of bending strength was observed. Analysis of the diagram of corrosion susceptibility of the mortars (relation of strength in corrosive media to the strength in water) shows that mortars containing 10% FBCC exhibit even 30% increase of bending strength in chloride solutions and 15% in sulfate solutions,

– the strength of mortars containing 20% FBCC is practically identical irrespective of the aggressive medium involved.

Conclusions

1. Spent fluidized bed cracking catalyst, used in amounts up to 20%, is a good pozzolana additive to Portland cement, increasing its water impermeability. The effect was confirmed in analytical, thermogravimetric, infrared absorption, and capillary elevation studies.
2. Short term storage of FBCC-containing mortars in municipal water and in solutions of sulfates and chlorides exhibited a leaching effect of water, particularly of concentrated solutions of chlorides. The presence of sulfates inhibited the leaching of $Ca(OH)_2$.
3. In the times of contact and concentrations studied the effects of the presence of Cl^- and SO_4^{2-} were similar: a small decrease of compressive strength and a small increase of bending strength of the mortars were observed. A susceptibility to corrosion was observed only in a decrease of compressive strength in mortars containing 10% addition of FBCC. In the bending strength tests even a small increase was observed. The strength of mortars containing 20% additions of FBCC was practically identical irrespective of the kind of aggressive medium used.

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